Constructing a bifunctional MoO_2/Co heterojunction for efficient electrocatalytic hydrogen evolution and hydrazine oxidation

Yuhao Guo,[a] Xiaolei Liu,[a] Yanmei Zang,[b] Yaqiang Wu,[a] Qianqian Zhang,[a] Zeyan Wang,[a] Yuanyuan Liu,[a] Zhaoke Zheng,[a] Hefeng Cheng,[a] Baibiao Huang,[a] Ying Dai,[b] Peng Wang,[a,*]

[a] State Key Lab of Crystal Materials, Shandong University, Jinan 250100, China

[b] School of Physics, Shandong University, Jinan 250100, China

*Corresponding author's e-mail address: pengwangicm@sdu.edu.cn (P. Wang)

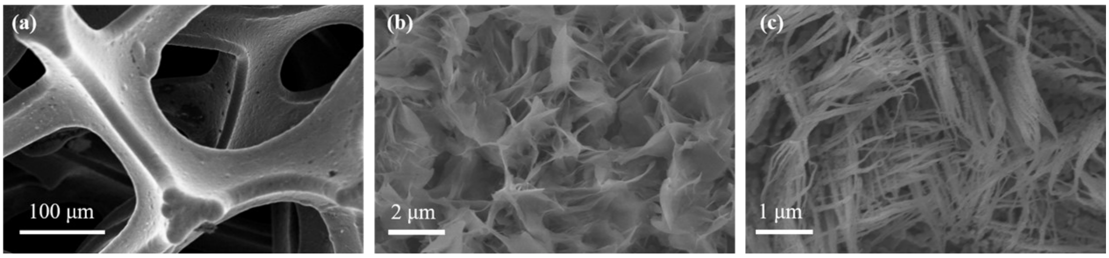

Figure. S1 SEM images of bare NF (a), CoMo precursor (b) and Co (c).

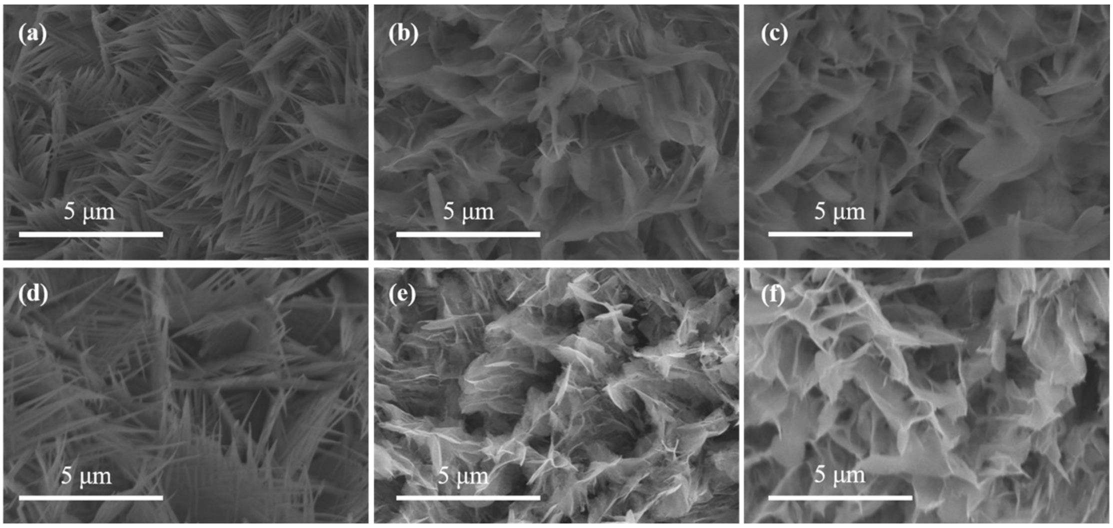

Figure. S2 SEM images of CoMo precursor-1h (a), CoMo precursor-3h (b), CoMo precursor-6h (c), MoO_2/Co-1h (d), MoO_2/Co-3h (e) and MoO_2/Co-6h (f).

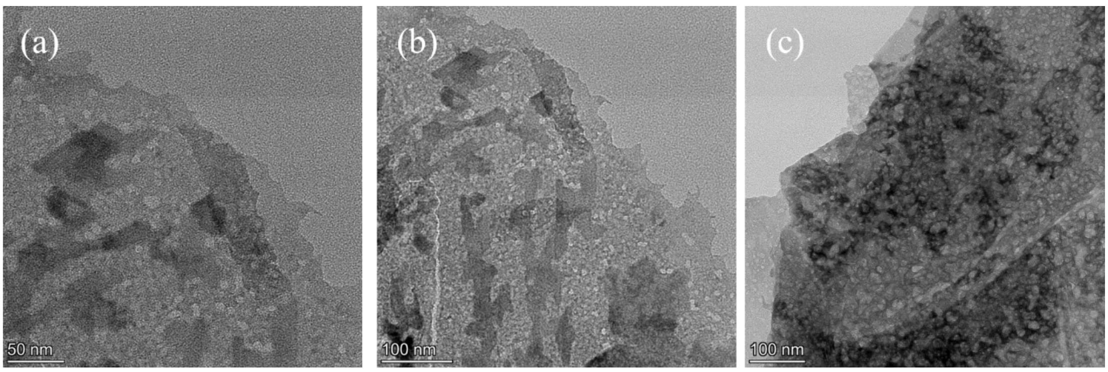

Figure. S3 TEM images of MoO_2/Co.

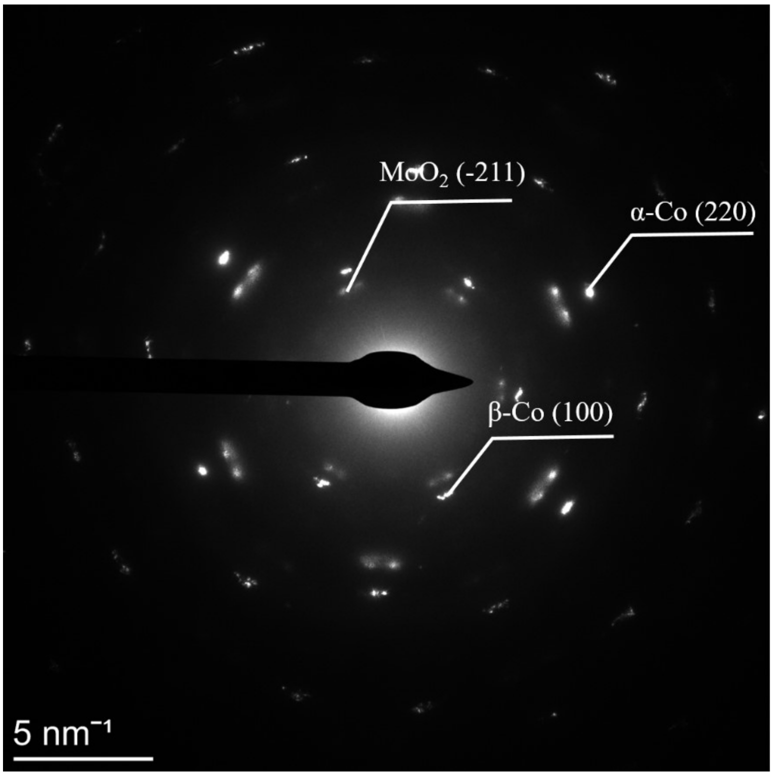

Figure. S4 SAED pattern of MoO_2/Co.

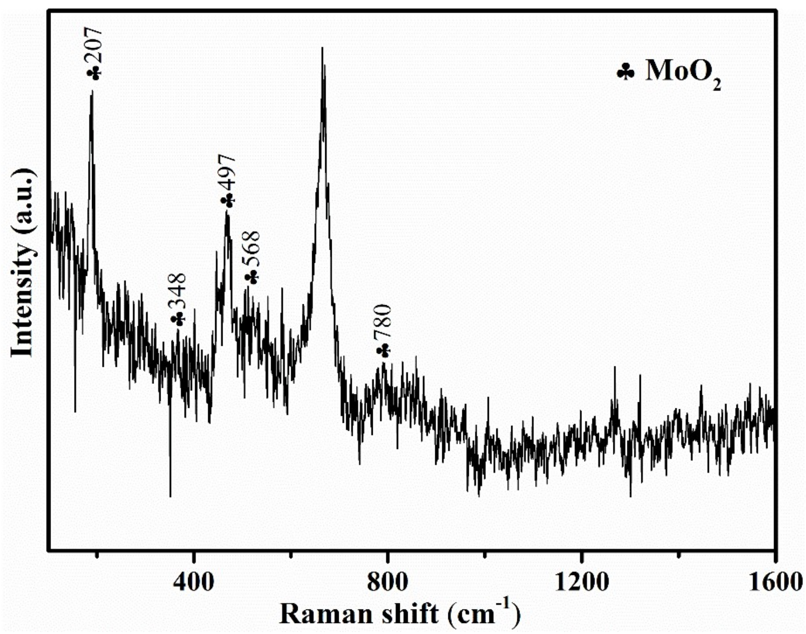

Figure. S5 Raman spectrum of MoO_2/Co.

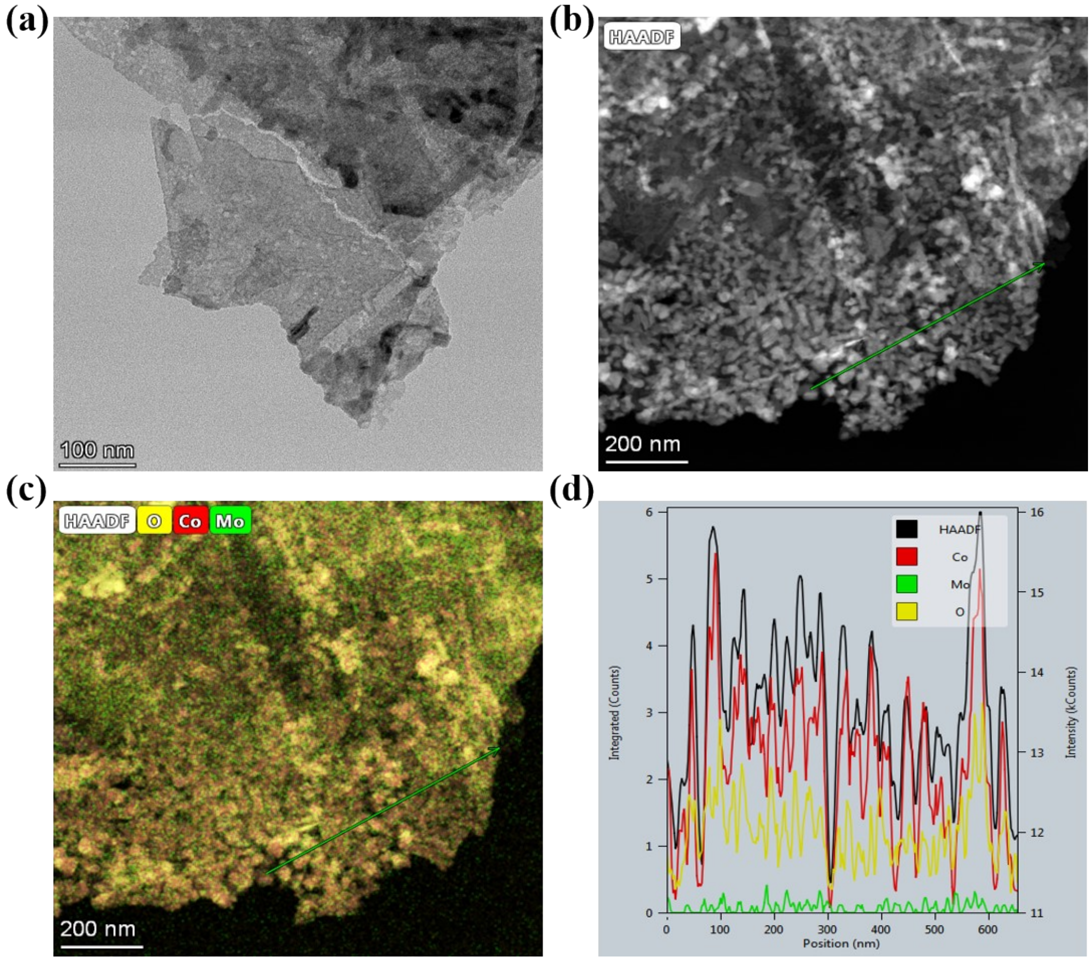

Figure. S6 (a) TEM image of MoO_2/Co; (b-d) EDS line scanning images of MoO_2/Co.

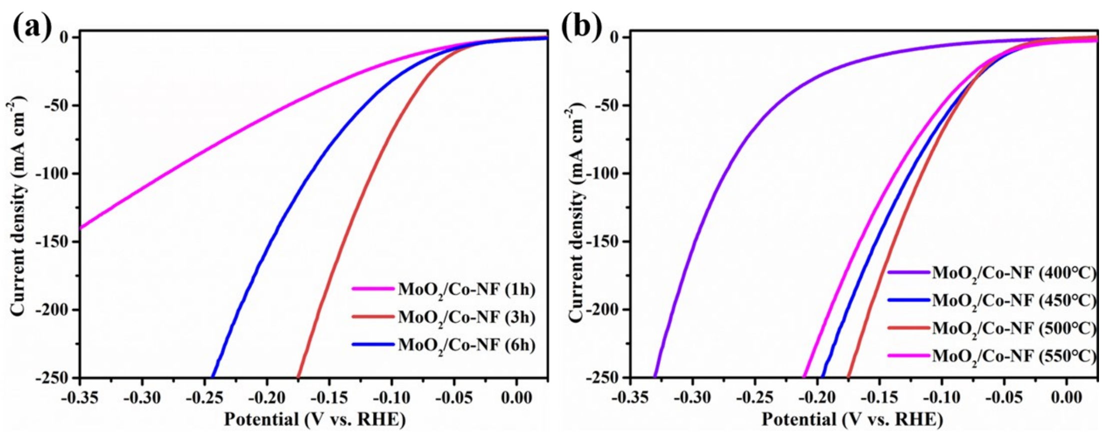

Figure. S7 LSV curves of MoO_2/Co-NF with different hydrothermal times (a) and different hydrogenation temperatures (b) in 1.0 M KOH solution.

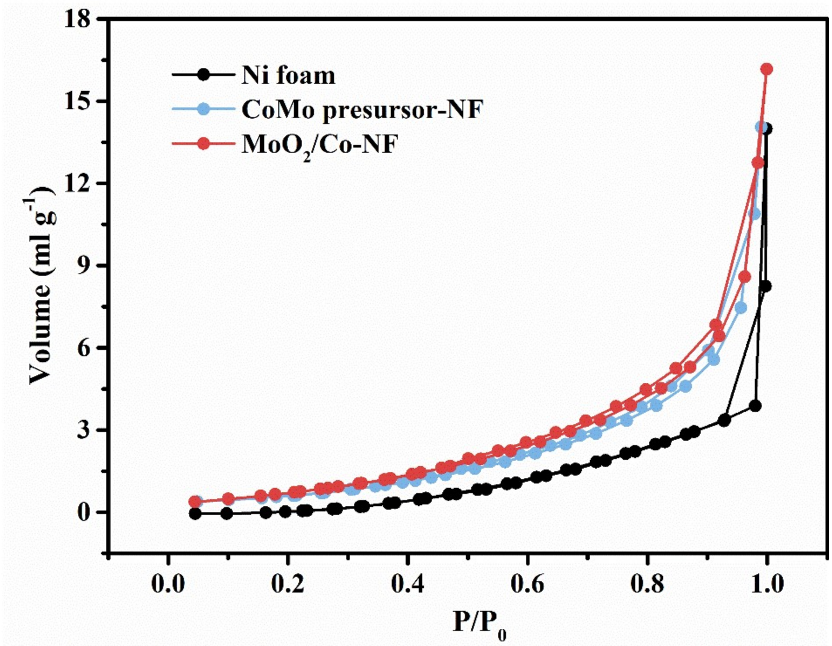

Figure. S8 BET results of the Ni foam, CoMo precursor-NF and MoO_2/Co-NF electrodes (sample: active material together with Ni foam substrate).

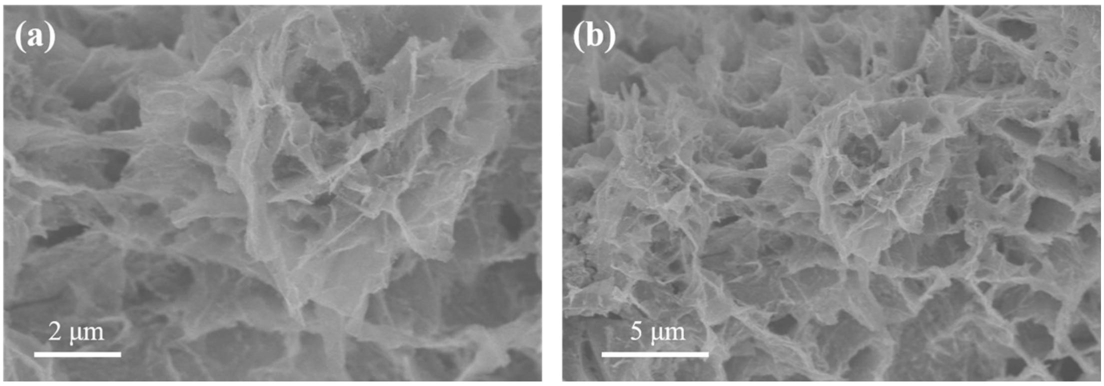

Figure. S9 SEM images of MoO_2/Co after 3000 cycles for HER.

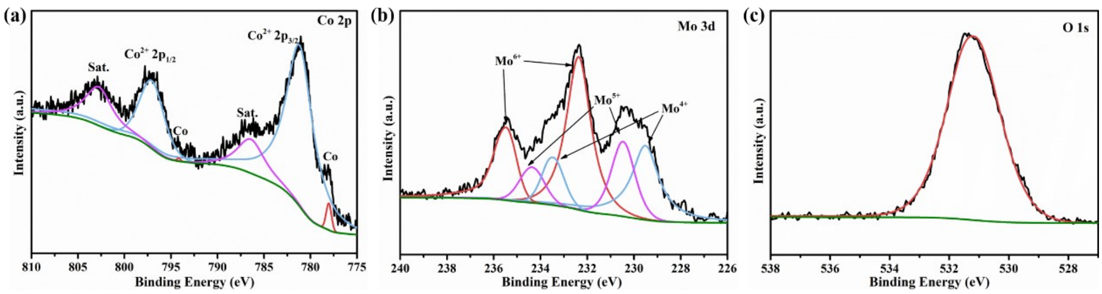

Figure. S10 XPS survey spectra of MoO_2/Co after 3000 cycles for HER.

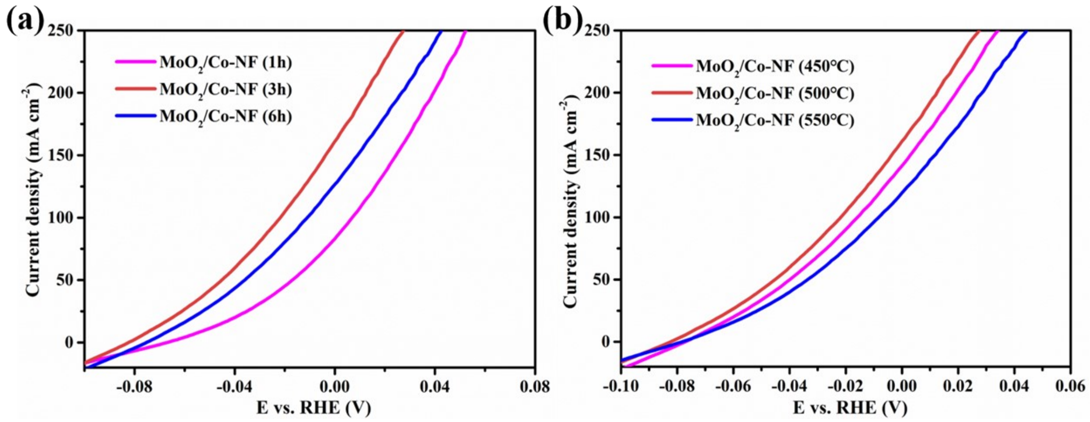

Figure. S11 LSV curves of MoO_2/Co-NF with different hydrothermal times (a) and different hydrogenation temperatures (b) in 1.0 M KOH with 0.5 M N_2H_4 solution.

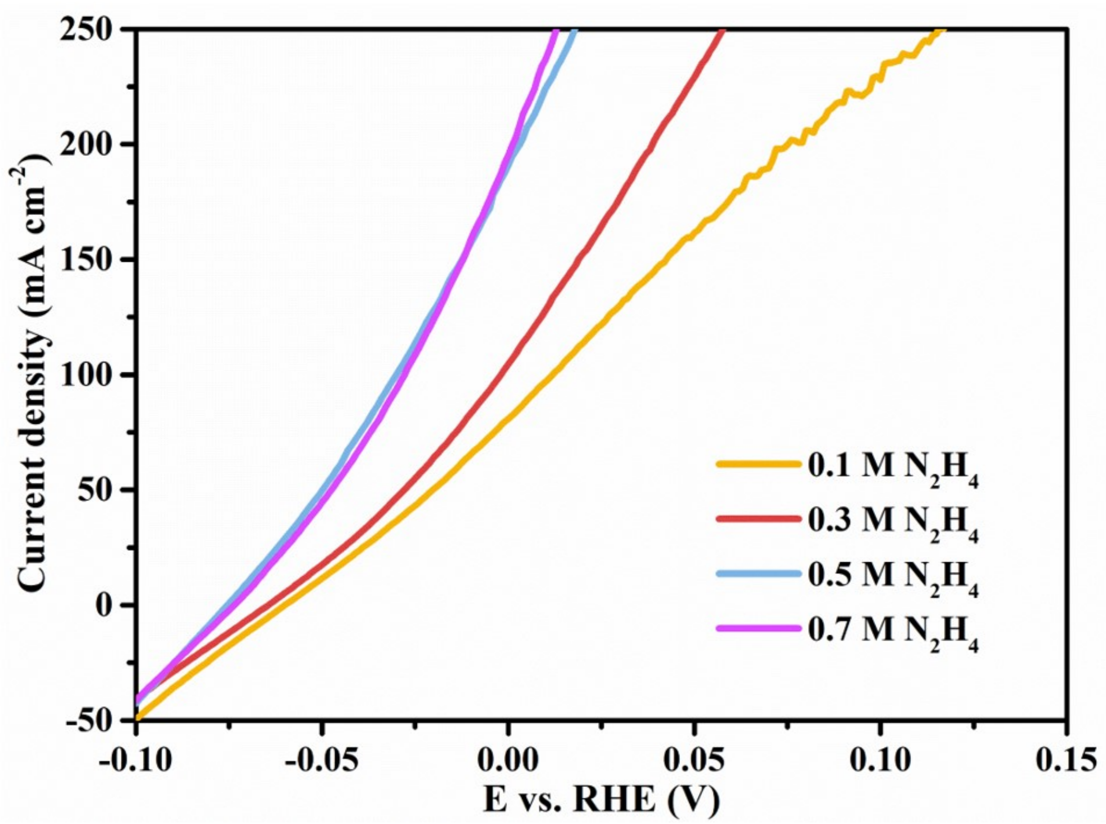

Figure. S12 LSV curves of MoO_2/Co-NF with different concentrations of N_2H_4 in 1M KOH.

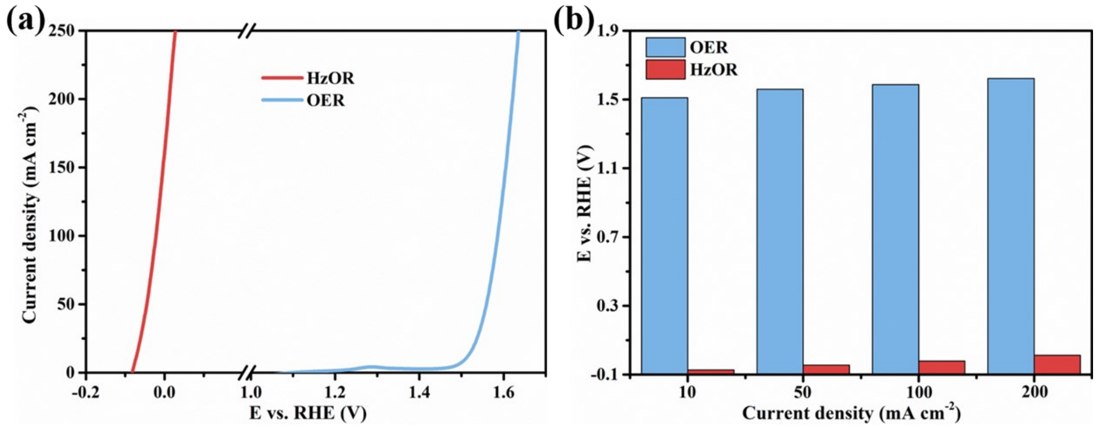

Figure. S13 LSV curves (a) and potentials (b) of MoO_2/Co-NF for OER and HzOR.

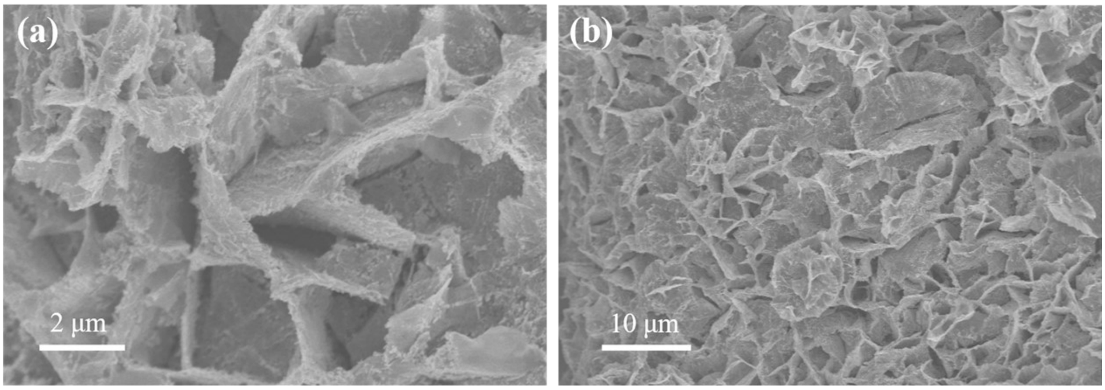

Figure. S14 SEM images of MoO_2/Co after 3000 cycles for HzOR.

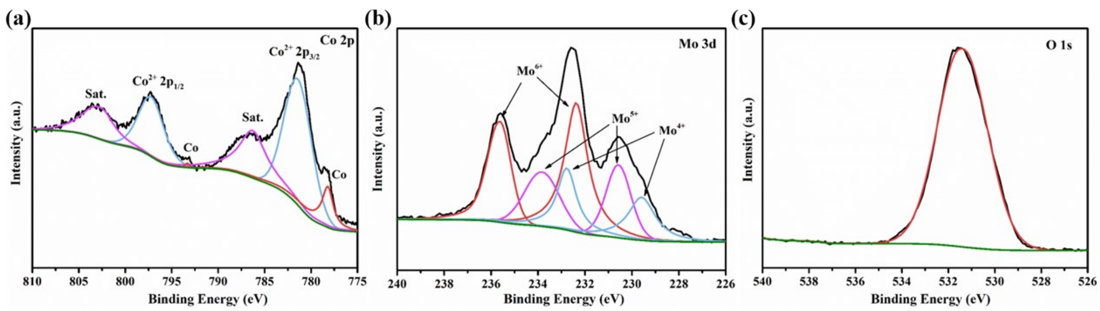

Figure. S15 XPS survey spectra of MoO_2/Co after 3000 cycles for HzOR.

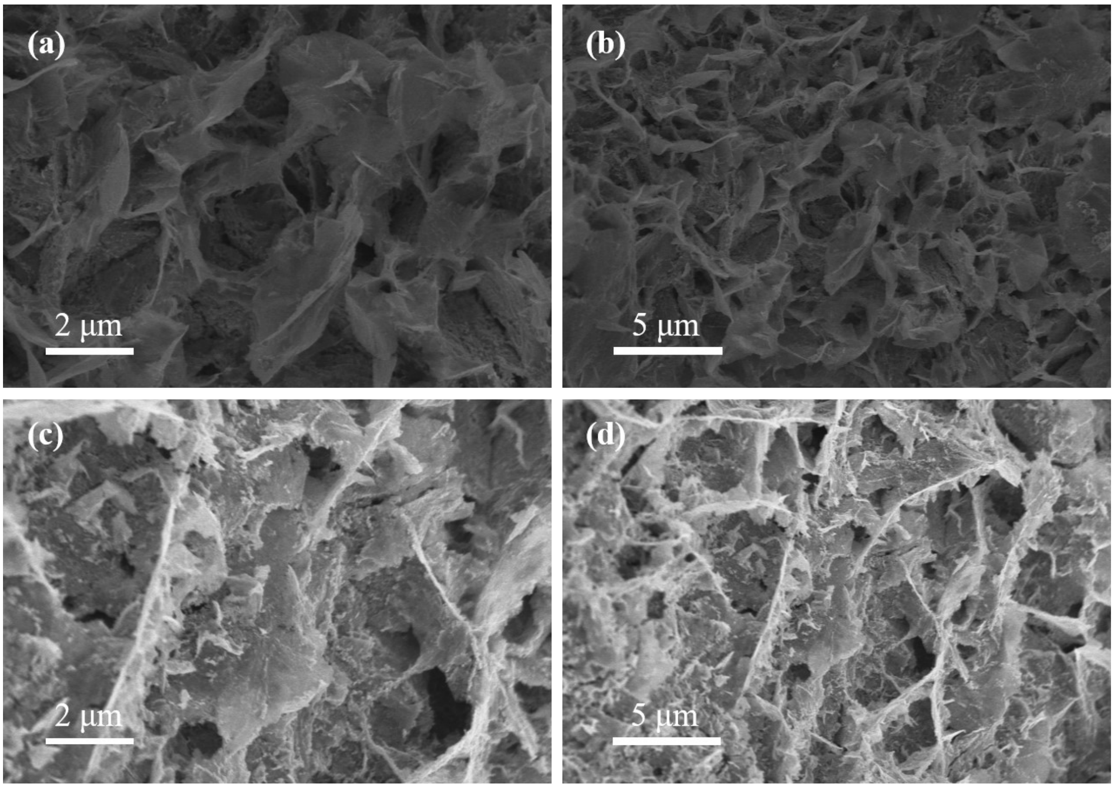

Figure. S16 SEM images of MoO_2/Co after 50 hours stability test for HER (a,b) and HzOR (c,d).

Table. S1 The element Inductive Coupled Plasma (ICP) characterization after different hydrothermal time.

Sample	Co/Mo (at.)
MoO_2/Co-1h	19.94:1
MoO_2/Co-3h	5.558:1
MoO_2/Co-6h	4.076:1

Table. S2 Comparison of HER activity in 1 M KOH for MoO_2/Co with other recently reported HER electrocatalysts.

Catalysts	η_{10}	Tafel slope (mV dec^{-1})	Reference
MoO_2/Co-NF	48	49.5	This work
Co_2P/CoN-in-NCNTs	98	57.0	[1]
Fe-CoS_2	40	32	[2]
NiCoN/C	103	N/A	[3]
V-Co_4N	37	44	[4]
PW-Co_3N	41	40	[5]
$CoSe_2$	79	84	[6]
Cr-Co_4N	21	38.1	[7]
Co-Ni_3N	194	156	[8]
Ni_3N/MoO_2	21	46	[9]
MoO_2/Ni	50.48	65.52	[10]
MoO_2-Ni NWs	58.4	36.6	[11]

Table. S3 Comparison of the HzOR performance of MoO_2/Co with other recently reported advanced catalysts. E_{10} is the HzOR working potential at 10 mA cm^{-2}.

Catalysts	Electrolyte	E_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
MoO_2/Co-NF	1.0 M KOH+0.5 M N_2H_4	-73	22.9	This work
PW-Co_3N	1.0 M KOH+0.1 M N_2H_4	-55	14	[5]
Fe-CoS_2	1.0 M KOH+0.1 M N_2H_4	-5	48	[2]
$CoSe_2$	1.0 M KOH+0.5 M N_2H_4	-17	N/A	[6]
Ni NCNAs	1.0 M KOH+0.3 M N_2H_4	-26	32.6	[12]
Mo-Ni_3N/Ni/NF	1.0 M KOH+0.1 M N_2H_4	-0.3	48	[13]
Ni_3N-Co_3N	1.0 M KOH+0.1 M N_2H_4	-88	21.6	[14]
RP-CPM	1.0 M KOH+0.3 M N_2H_4	-70	47.6	[15]
Ni_2P/NF	1.0 M KOH+0.5 M N_2H_4	-65	55	[16]
Ni-C HNSA	1.0 M KOH+0.1 M N_2H_4	-20	16.2	[17]

Table. S4 Comparison of OHzS of MoO_2/Co with other reported catalysts. E_{10} is the OHzS working potential at 10 mA cm^{-2}.

Catalysts	Electrolyte	E_{10} (mV)	Stability	Reference
MoO_2/Co-NF	1.0 M KOH+0.5 M N_2H_4	35	50 h	This work
PW-Co_3N	1.0 M KOH+0.1 M N_2H_4	358	20 h	[5]
$CoSe_2$	1.0 M KOH+0.5 M N_2H_4	164	14 h	[6]
Ni NCNAs	1.0 M KOH+0.3 M N_2H_4	79 (E_{50})	N/A	[12]
Mo-Ni_3N/Ni/NF	1.0 M KOH+0.1 M N_2H_4	55	10 h	[13]
Ni_3N-Co_3N	1.0 M KOH+0.1 M N_2H_4	71	20 h	[14]
RP-CPM	1.0 M KOH+0.3 M N_2H_4	353	20 h	[15]
Ni_2P/NF	1.0 M KOH+0.5 M N_2H_4	1.0V(E_{500})	10 h	[16]
Ni-C HNSA	1.0 M KOH+0.1 M N_2H_4	140 (E_{50})	30 h	[17]

Reference

[1] Y.Y. Guo, P.F. Yuan, J.A. Zhang, H.C. Xia, F.Y. Cheng, M.F. Zhou, J. Li, Y.Y. Qiao, S.C. Mu, Q. Xu, Adv Funct Mater, 28 (2018).

[2] X.J. Liu, J. He, S.Z. Zhao, Y.P. Liu, Z. Zhao, J. Luo, G.Z. Hu, X.M. Sun, Y. Ding, Nat Commun, 9 (2018).

[3] J.P. Lai, B.L. Huang, Y.G. Chao, X. Chen, S.J. Guo, Adv Mater, 31 (2019).

[4] Z.Y. Chen, Y. Song, J.Y. Cai, X.S. Zheng, D.D. Han, Y.S. Wu, Y.P. Zang, S.W. Niu, Y. Liu, J.F. Zhu, X.J. Liu, G.M. Wang, Angew Chem Int Edit, 57 (2018) 5076-5080.

[5] Y. Liu, J.H. Zhang, Y.P. Li, Q.Z. Qian, Z.Y. Li, Y. Zhu, G.Q. Zhang, Nat Commun, 11 (2020).

[6] J. Qi, W. Zhang, R. Cao, Adv Energy Mater, 8 (2018).

[7] N. Yao, P. Li, Z.R. Zhou, Y.M. Zhao, G.Z. Cheng, S.L. Chen, W. Luo, Adv Energy Mater, 9 (2019).

[8] C.R. Zhu, A.L. Wang, W. Xiao, D.L. Chao, X. Zhang, N.H. Tiep, S. Chen, J.N. Kang, X. Wang, J. Ding, J. Wang, H. Zhang, H.J. Fan, Adv Mater, 30 (2018).

[9] S.W. Niu, Y.Y. Fang, J.B. Zhou, J.Y. Cai, Y.P. Zang, Y.S. Wu, J. Ye, Y.F. Xie, Y. Liu, X.S. Zheng, W.G. Qu, X.J. Liu, G.M. Wang, Y.T. Qian, J Mater Chem A, 7 (2019) 10924-10929.

[10] W.L. Liang, P.Y. Dong, Z.C. Le, X.Y. Lin, X.Y. Gong, F.Y. Xie, H. Zhang, J. Chen, N. Wang, Y.S. Jin, H. Meng, Acs Appl Mater Inter, 13 (2021) 39470-39479.

[11] X. Liu, K. Ni, C.J. Niu, R.T. Guo, W. Xi, Z.Y. Wang, J.S. Meng, J.T. Li, Y.W. Zhu, P.J. Wu, Q. Li, J. Luo, X.J. Wu, L.Q. Mai, Acs Catal, 9 (2019) 2275-2285.

[12] Z.B. Liang, T.J. Qiu, S. Gao, R.Q. Zhong, R.Q. Zou, Adv Energy Mater, (2021).

[13] Y. Liu, J.H. Zhang, Y.P. Li, Q.Z. Qian, Z.Y. Li, G.Q. Zhang, Adv Funct Mater, 31 (2021).

[14] Q.Z. Qian, J.H. Zhang, J.M. Li, Y.P. Li, X. Jin, Y. Zhu, Y. Liu, Z.Y. Li, A. El-Harairy, C. Xiao, G.Q. Zhang, Y. Xie, Angew Chem Int Edit, 60 (2021) 5984-5993.

[15] Y.P. Li, J.H. Zhang, Y. Liu, Q.Z. Qian, Z.Y. Li, Y. Zhu, G.Q. Zhang, Sci Adv, 6

(2020).
[16] C. Tang, R. Zhang, W.B. Lu, Z. Wang, D.N. Liu, S. Hao, G. Du, A.M. Asiri, X.P. Sun, Angew Chem Int Edit, 56 (2017) 842-846.
[17] Y. Zhu, J.H. Zhang, Q.Z. Qian, Y.P. Li, Z.Y. Li, Y. Liu, C. Xiao, G.Q. Zhang, Y. Xie, Angew Chem Int Edit, (2021).